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## Stabilizing Dielectric Constants of Fluorine-Doped SiO<sub>2</sub> Films by N<sub>2</sub>O-Plasma Annealing

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### ABSTRACT

Fluorine-doped SiO<sub>2</sub> (FSG) has a low dielectric constant just after deposition. However, the dielectric constant of FSG gradually increases with time when left in air. We have developed a way to stabilize dielectric constants of FSG left in the air by plasma annealing. We have found that N<sub>2</sub>O-plasma annealing is quite effective for blocking moisture. The dielectric constants of FSG treated by the N<sub>2</sub>O-plasma annealing rarely change.

### Introduction

With increasing integration density of large scale integrated (LSI) devices, multilevel metallization technology is becoming more important than it used to be. In advanced logic devices, the interlayer dielectrics have increased to four or five layers. Strong improvements are required on these interlayer dielectrics; for example, good gap filling, global planarization, high resistance to moisture and low outgassing.<sup>1-3</sup> We think that in the near future it will be an important issue as to how to lower the dielectric constants of interlayer dielectrics<sup>4,5</sup> to solve a problem that we are beginning to confront now, that is, wiring delay which is beginning to dominate the total signal delay in LSIs. Many research groups are trying to develop fluorine-doped SiO<sub>2</sub> (FSG) to realize such an ideal interlayer dielectric with a low dielectric constant. We also have been developing FSG. We have achieved a low dielectric constant, as low as 3.6, in a practical sense, however, the most critical issue in FSG, with lower dielectric constants was the low resistance to moisture. If FSG was left in the air (temperature: 23°C, humidity: 42%), FSG absorbed moisture easily which resulted in an increase of the dielectric constant, because the dielectric constant of H<sub>2</sub>O is as high as 80 at room temperature. Worse still it has a bad influence for device reliability through postthermal processes. However, we have found the clue for solving this problem by N<sub>2</sub>O plasma annealing.

### Experimental

FSG films were deposited at 400°C on Si substrates by plasma enhanced chemical vapor deposition (PECVD: AMAT, Model P-5000C Delta mf tetraethylorthosilicate (TEOS) version, for 8 in.). Dual frequencies (13.56 MHz and 350 kHz) were applied simultaneously to the electrode. A C<sub>2</sub>F<sub>4</sub> gas was introduced into the chamber as a source gas of fluorine in addition to TEOS and O<sub>2</sub>. A scheme of the PECVD reactor is shown in Fig. 1. The FSG films were annealed by O<sub>2</sub>, N<sub>2</sub>, or N<sub>2</sub>O plasmas with another PECVD chamber after the deposition. The deposition condition is shown in Table I and the plasma annealing condition is shown in Table II.

We studied changes in dielectric constants, as a function of time, to learn the effects of plasma annealing with O<sub>2</sub>, N<sub>2</sub>, or N<sub>2</sub>O plasmas, and also to investigate the effects of plasma annealing on the molecular structures of the FSG films. The dielectric constants of the FSG films were measured in the following way. The FSG films were deposited on heavily ion implanted Si substrates. The heavy ion implantation, more than 10<sup>16</sup>/cm<sup>2</sup>, was necessary for completely suppressing depletion layers on the surfaces of Si substrates and thereby for assuring correct measurements of dielectric constants of FSG. Then Au was evaporated on the FSG films as electrodes, and the capacitance of each MOS structure was measured. The thickness was measured by ellipsometry. The dielectric constants were calculated from the capacitance, the thickness, and the area of the electrode. To assure ohmic contacts between the back side of Si substrates and the stage of the probe, Ag paste was coated on the back side of Si substrates.

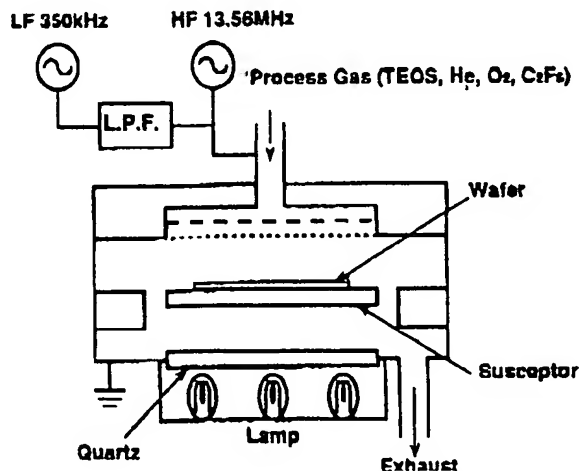


Table I. Deposition condition of PSG films.

Sample	Gas flow rate (sccm)			Temperature (°C)	Pressure (Torr)	Plasma power (W) HF/LF
	TEOS (He)	O <sub>2</sub>	C <sub>2</sub> F <sub>4</sub>			
PSG	480	700	350	400	5	80/90

Table II. Annealing conditions.

Annealing	Gas	Plasma power (W) HF/LF	Flow rate (sccm)	Temperature (°C)	Pressure (Torr)
N <sub>2</sub> O-plasma annealing	N <sub>2</sub> O	300/0	500	400	4
N <sub>2</sub> -plasma annealing	N <sub>2</sub>	300/0	500	400	4
O <sub>2</sub> -plasma annealing	O <sub>2</sub>	300/0	500	400	4
O <sub>2</sub> -gas annealing	O <sub>2</sub>	0/0	500	400	4

The wet etching rates as a function of film depth, Fourier transform infrared (FTIR) spectra, and thermal desorption spectroscopy (TDS) spectra were examined in order to investigate differences in the chemical properties between FSG films before and after the plasma annealing. The wet etching rates were measured by dissolving films with 5% hydrofluoric acid (HF) step by step and by measuring the thickness at each step. FTIR spectra were taken before and after the N<sub>2</sub>O-plasma annealing. FTIR spectra were taken by subtracting the signals of Si substrates from those of FSG films deposited on the Si substrates. TDS spectra of samples before annealing were taken after 24 h from the deposition, and TDS spectra of samples treated by the N<sub>2</sub>O-plasma annealing were observed after 24 h from the annealing. These measurements were done from 30 to 1000°C raising temperature by 1°C per second.

Secondary ion mass (SIMS) spectra were taken to investigate changes in chemical composition of FSG films as a function of depth after the N<sub>2</sub>O plasma annealing, and also to investigate difference between the N<sub>2</sub>O-plasma and O<sub>2</sub>-plasma annealing.

### Results and Discussion

Figure 2 shows the change in dielectric constants as a function of time. In this experiment, three samples were

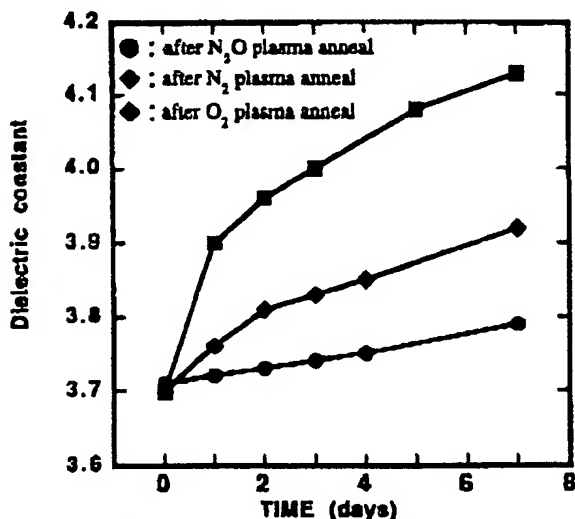


Fig. 2. Change in dielectric constants as a function of time.

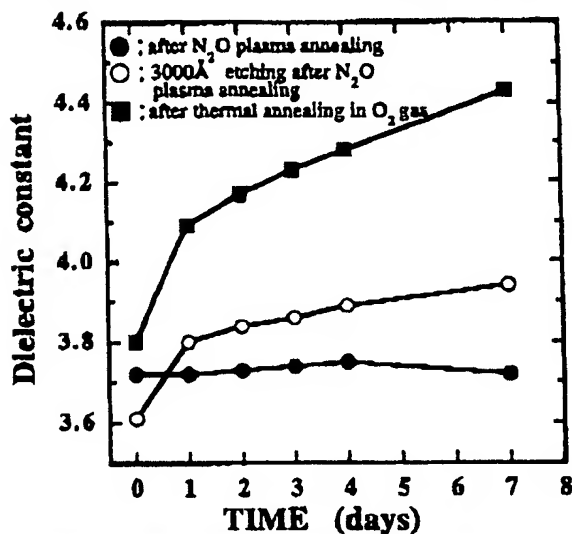


Fig. 3. Change in dielectric constants as a function of time.

used; sample 1 was annealed in an O<sub>2</sub> plasma, sample 2 was annealed in an N<sub>2</sub> plasma, and sample 3 was annealed in an N<sub>2</sub>O plasma. In every case, the plasma annealing time was 1 min. The dielectric constant of FSG after the O<sub>2</sub>-plasma annealing goes up with time. However, the increase of dielectric constants of FSG after N<sub>2</sub>-plasma annealing or N<sub>2</sub>O-plasma annealing was smaller than that after O<sub>2</sub>-plasma annealing, especially the latter was very small. As for the increase of dielectric constants with the passage of time, it is assumed that it comes from absorbing moisture. Comparing these results, it is suggested that nitrogen atoms in the plasma play an important role in making FSG films highly resistant to moisture. N<sub>2</sub>O plasma is more effective than N<sub>2</sub> plasma. It is thought that this result is due to the difference of decomposition efficiency in plasmas, i.e., the decomposition efficiency of N<sub>2</sub>O is higher than that of N<sub>2</sub>.

Figure 3 also shows change in dielectric constants as a function of time. In this experiment, three samples were used; sample 1 was annealed in O<sub>2</sub> gas at 400°C, sample 2 was annealed in an N<sub>2</sub>O plasma, and sample 3 was etched by 3000 Å after annealing in N<sub>2</sub>O plasma. In every case, the annealing time was 30 min. The dielectric constant of

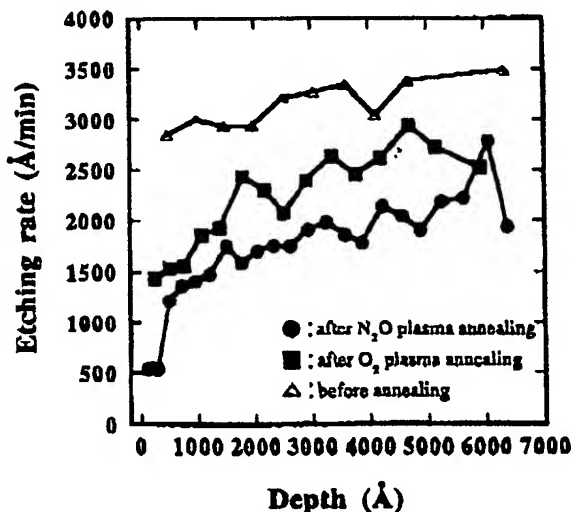


Fig. 4. Etching rate of FSG films as a function of film depth.

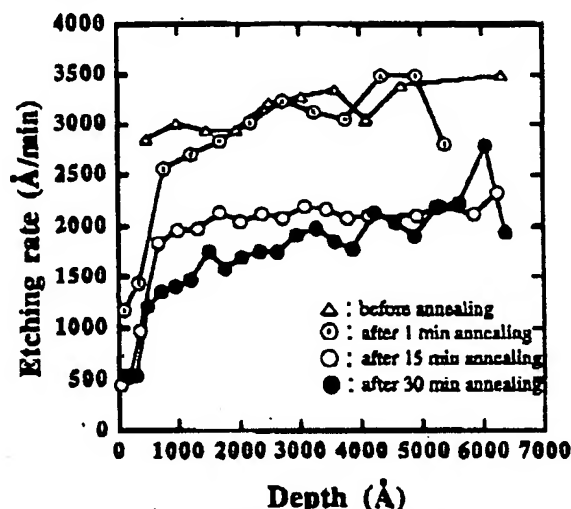


Fig. 5. Etching rate of FSG films as a function of film depth.

FSG after  $O_2$  gas annealing goes up with the passage of time. However, as mentioned above, the dielectric constant of FSG after  $N_2O$ -plasma annealing rarely changes. Especially was the dielectric constant of the same sample, but etched after annealing in  $N_2O$  plasma, kept constant. These results suggest the following. Thirty minutes of treatment by  $N_2O$  plasma is long enough to make FSG films highly resistant to moisture. However, the dielectric constant of the sample etched by 3000 Å after  $N_2O$ -plasma annealing goes up a little with the passage of time. This indicates that the improvement in the quality of FSG films is not uniform through the film. In other words, the surface of FSG films treated by  $N_2O$  plasma seems to be more hydrophobic than the inside, though the quality of the inside is also improved by the  $N_2O$ -plasma treatment.

Figure 4 shows etch rates of FSG as a function of film depth before annealing, after  $O_2$ -plasma annealing, and after  $N_2O$ -plasma annealing for 30 min. The etch rate of nonannealed sample increased a little bit with depth. The etch rate of  $O_2$ -plasma annealed sample became a little bit faster with increased depth than in the case of the nonannealed sample, but it was about two-thirds of the etching rate of the nonannealed sample. The etch rate of the  $N_2O$ -plasma annealed sample was smaller than that of  $O_2$ -plasma annealed sample. In the case of the  $N_2O$ -plasma annealed sample, the etch rate near the surface was less than half of that of the inside. These results indicate that (i) chemical properties in the inside of FSG films were changed by  $N_2O$ -plasma annealing and (ii) chemical properties at the surface of FSG films were changed more strongly than that in the inside.

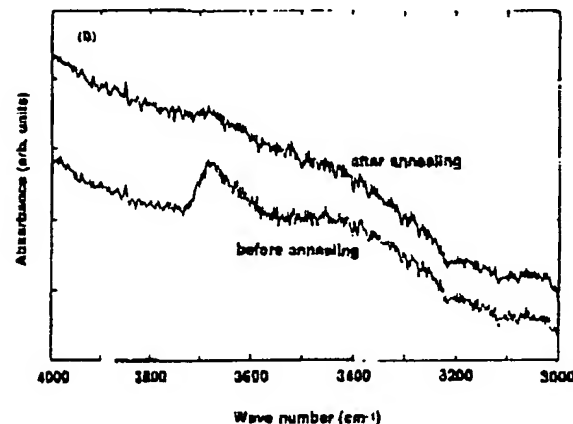
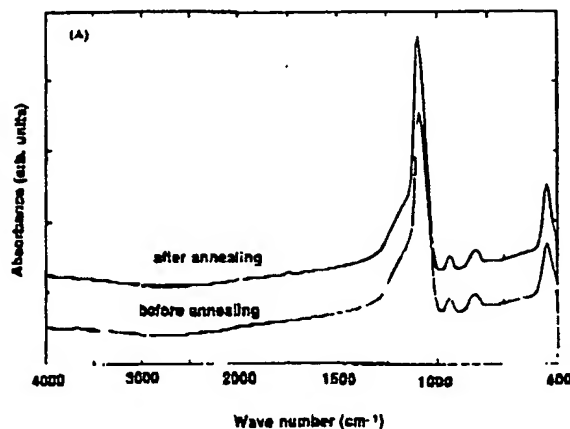
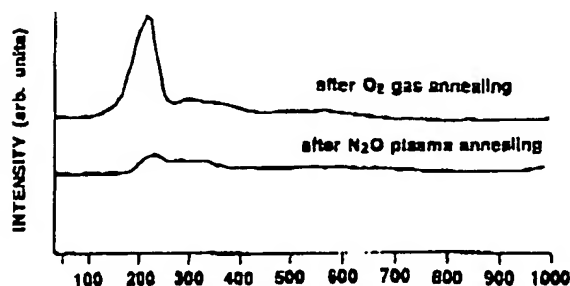
Fig. 7. FTIR spectra of FSG films before and after  $N_2O$ -plasma annealing: (A) in the range from 400 to 4000  $cm^{-1}$ ; (B) in the range from 3000 to 4000  $cm^{-1}$ .

Figure 5 shows etch rates of FSG before and after  $N_2O$ -plasma annealing as a function of the film depth for different annealing time. In the case of annealing as short as 1 min, the etch rate in the inside was the same as that of the nonannealed sample, while in the case of the 15 min annealing, the etch rate in the inside was lower than that of the nonannealed sample, suggesting that the reaction proceeded to the deeper part of the film during the prolonged treatment time. Moreover, in a case of the 30 min annealing, the etching rate in the inside was a little bit lower than that of the 15 min annealed sample. The etch rates near the surface of these two samples (i.e., 15 and 30 min) were almost the same, and they are a little bit lower than that of the 1 min annealed sample. It is thought from these results that changing the chemical properties in the inside of FSG films strongly depends on annealing time, while changing the chemical properties at the surface does not depend on annealing time so much, suggesting that the reaction is diffusion limited. Comparing the data of the  $N_2O$ -plasma annealed sample with that of the  $O_2$ -plasma annealed sample, it is thought that properties in the inside of FSG films were improved by  $N_2O$ -plasma annealing more than by  $O_2$ -plasma annealing, but  $O_2$ -plasma annealing is also somewhat effective in improving the properties in the inside of the FSG films. On the other hand, the properties at the surface of FSG films were improved only by  $N_2O$ -plasma annealing.  $O_2$ -plasma

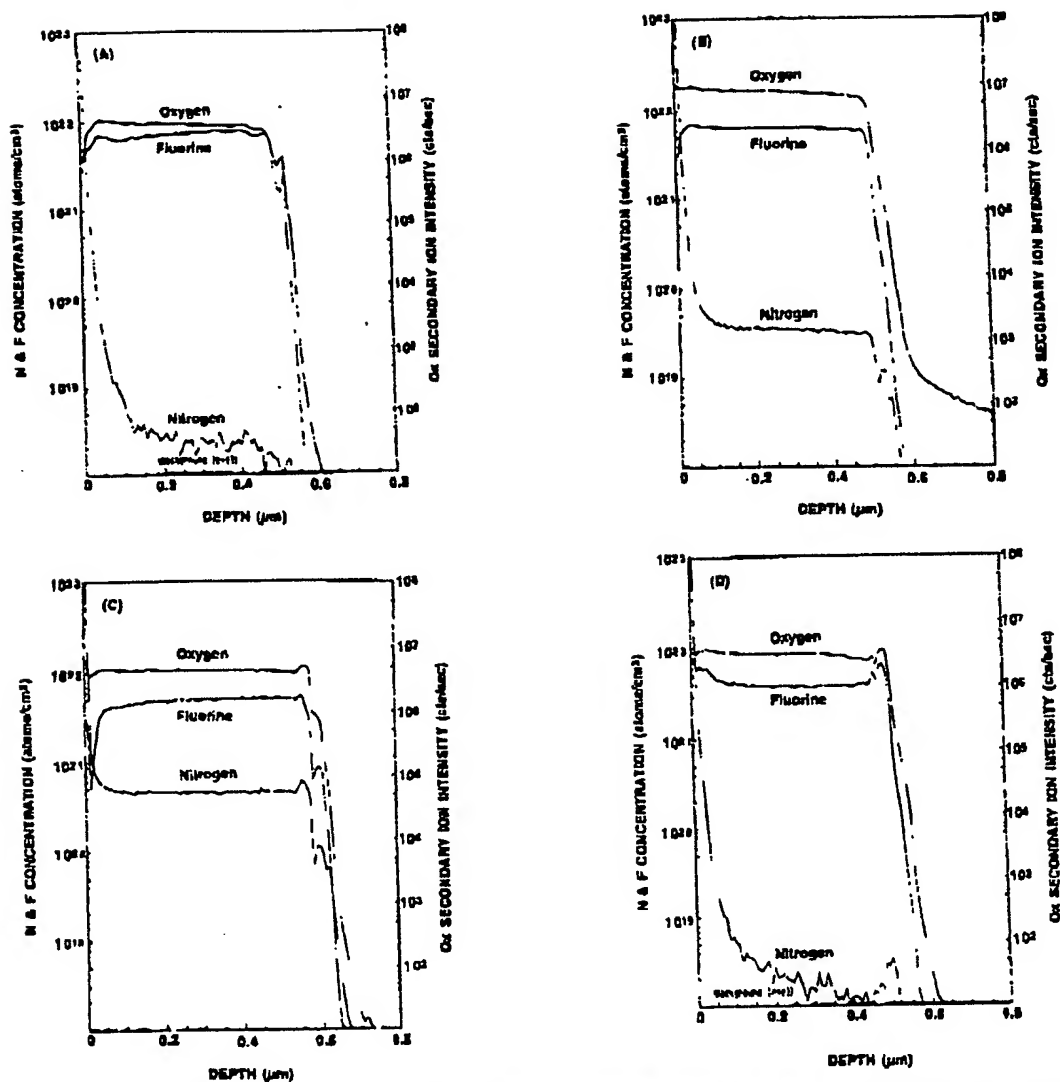


Fig. 8. SIMS spectra of FSG films: (A) before annealing; (B) after  $N_2O$ -plasma annealing for 1 min; (C) after  $N_2O$ -plasma annealing for 15 min; (D) after  $O_2$ -plasma annealing for 1 min.

from specimens left in the air 24 h after the annealing. These spectra suggest that the quantity of moisture absorption after  $N_2O$ -plasma annealing is much lower than that after  $O_2$ -gas annealing. A broad peak ranging from about 100 to about  $250^\circ C$  is considered to be due to physically absorbed  $H_2O$  molecules in the film left in the air after the deposition, suggesting that the  $N_2O$ -plasma annealing is effective against moisture absorption.

Figure 7 shows FTIR spectra of FSG before and after  $N_2O$ -plasma annealing. After  $N_2O$ -plasma annealing,  $H-OH$  and  $Si-OH$ <sup>11</sup> peaks were reduced and the  $Si-O$  peak became larger. The peak due to  $Si-O$  bonds became larger after  $N_2O$ -plasma annealing. These results seem to be caused by oxidation of FSG films in the plasma. Other discernible differences between  $N_2O$ -plasma annealed and nonannealed samples were not observed in the FTIR spectra.<sup>8-11</sup>

Figure 8 shows SIMS spectra of FSG films before annealing, after  $O_2$ -plasma annealing, and after  $N_2O$ -plasma annealing. We found that the atomic density of fluorine in the inside has a tendency to decrease after plasma annealing. The decrease in the atomic density of fluorine in the inside was larger after  $O_2$ -plasma annealing than after  $N_2O$ -plasma annealing. With shortened plasma

time due to  $N_2O$  plasma became nondetectable as compared with  $O_2$ -plasma annealing. Another important phenomenon we need to emphasize here is the existence of nitrogen atoms after  $N_2O$ -plasma annealing for both the case of 1 and 15 min annealing. Comparing the data between  $N_2O$ -plasma and  $O_2$ -plasma annealed samples, we think that there might be two origins for making FSG films highly resistant to moisture absorption. One is the existence of nitrogen atoms in the films, the other is changing the chemical composition at the surface. That is, it is thought that a slight amount of nitride was formed through the inside,<sup>12</sup> while the thin top surface is closer to being pure nitride.<sup>13</sup>

Table III shows stress change of FSG films before annealing, after  $O_2$ -plasma annealing, and after  $N_2O$ -plasma annealing. We found that the stress of films changes to the tensile direction following plasma annealing. This tendency is stronger in  $N_2O$  plasma than in  $O_2$  plasma.

Summarizing the results of this research, we would conclude the following. By  $N_2O$ -plasma annealing, a small quantity of nitride is formed in the inside of FSG films and the sources of absorbing moisture (e.g.,  $Si-OH$ ) are removed. This is the reason why the wet etching rates of FSG films annealed by  $N_2O$ -plasma with HF become slow-

Table III. Stress of FSG films before and after plasma annealing using  $N_2O$  plasma or  $O_2$  plasma.

	Stress (dyn/cm <sup>2</sup> )	
	Before annealing	After annealing
$N_2O$ -plasma annealing	-6.2E8	-3.8E8
$O_2$ -plasma annealing	-6.3E8	-4.3E8

and why the dielectric constant of FSG after  $N_2O$ -plasma annealing rarely changes with the passage of time as compared with others. Further,  $N_2O$ -plasma annealing seems to change the chemical composition at the surface. Because of this change in the chemical composition at the surface and small amounts of nitride formed in the inside, FSG shows high resistance against moisture absorption if the plasma annealing time is long enough.

#### Conclusion

We found that the  $N_2O$ -plasma annealing of FSG is quite effective in blocking moisture. We feel that this method opens up the possibility for using FSG films in actual use. The effect of  $N_2O$ -plasma annealing is considered to be as follows. Oxygen atoms terminate dangling bonds and simultaneously oxidize Si-H<sub>2</sub> bonds in FSG films. Nitrogen atoms form small amounts of nitride through whole films and a little stronger nitride at the surface than the inside. In other words, the reason why  $N_2O$ -plasma annealing is effective in blocking moisture is that (i) the origin of moisture absorbing (i.e., Si-OH bonds) is

removed from the film and (ii) the surface becomes hydrophobic.

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## Processing of Three-Dimensional Microstructures Using Macroporous n-Type Silicon

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#### ABSTRACT

A process for micromachining arbitrary structures with high aspect ratios in bulk silicon utilizing standard micro-electronic processes is presented. It is based on electrochemical macropore formation on n-type silicon in electrolytes containing hydrofluoric acid. Very regular pore arrays with pore diameters and distances in the micrometer range and pore lengths of several hundred micrometers can be produced with this technique. Wafers with suitable prefabricated pore arrays are used as substrates for a micromachining process including anisotropic etching of very deep structures yielding straight walls to depths of as much as 150  $\mu\text{m}$ .

#### Introduction

Micromechanical technology has been developed for the preparation of simple, small structures and sensors in the micrometer range in the recent decade. Beyond that, the

for electroplating. A low cost alternative to the LIGA process is reported in Ref. 6. Neither of these techniques can be applied for direct silicon micromachining. Recently, a combined approach of lithographic and reactive ion etching (RIE) has been developed which can be

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